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Simultaneous detection of alkylamines in the surface ocean and atmosphere of the Antarctic sympagic environment

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Abstract

Measurements of alkylamines from seawater and atmospheric samples collected simultaneously across the Antarctic Peninsula, South Orkney and South Georgia Islands are reported. Concentrations of mono-, di- and trimethylamine (MMA, DMA and TMA, respectively), and their precursors, the quarternary amines glycine betaine and choline, were enhanced in sympagic sea water samples relative to ice-devoid pelagic ones, suggesting the microbiota of sea ice and sea ice-influenced ocean is a major source of these compounds. Primary sea-spray aerosol particles artificially generated by bubbling seawater samples were investigated by Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS) of single particles; their mixing state indicated that alkylamines were aerosolized with sea spray from dissolved and particulate organic nitrogen pools. Despite this unequivocal sea spray-associated source of alkylamines, ATOFMS analyses of ambient aerosols in the sympagic region indicated that the majority (75-89 %) of aerosol alkylamines were of secondary origin, i.e., incorporated into the aerosol after gaseous air-sea exchange. These findings show that sympagic seawater properties are a source of alkylamines influencing the biogenic aerosol fluxed from the ocean into the boundary layer; these organic nitrogen compounds should be considered when assessing secondary aerosol formation processes in Antarctica.

1. Introduction

The impact of aerosols on cloud droplet concentrations and hence on cloud optical properties is of paramount importance for global climate¹. Current climate models are particularly challenged in predicting the radiation budget, particularly the surface short wave radiation, over the Southern Ocean². Overestimates of surface heating result in errors in predicted sea surface temperature (SST) and ocean heat uptake³, thus affecting long term climate predictions⁴. The source of such a bias is thought to be a poor representation of clouds along with the underprediction of the aerosol optical depth, which suggests a hitherto overlooked source of aerosols influencing cloud properties in this region⁵. In a pristine environment like Antarctica and its surrounding ocean, where the atmosphere still exists in its natural state⁶, missing aerosol sources from natural processes may be overlooked. Uncertainties for modeling aerosol-cloud interactions and cloud radiative forcing in part arise from a poor source apportionment of natural aerosols including emissions of biogenic sulfur and sea spray⁷. The relative roles of secondary aerosols produced from biogenic sulfur versus primary sea-spray aerosols in regulating cloudiness above the Southern Ocean remains controversial⁸⁻¹³. The plankton-derived trace gas dimethylsulfide (DMS) has long been identified as a major source of non-sea-salt sulfate and methanesulfonate in newly formed and aged secondary aerosols, enhancing particle number and mass concentrations⁹. It is plausible that other organic aerosol components of biogenic origin may act similarly, contributing ingredients for aerosol formation and growth¹⁴. Moreover, there is growing evidence that sea spray does not only contribute sea salt particles to the aerosol pool, but organic matter with cloud-forming properties¹⁵. Despite the increasing awareness of their importance, measurements of organic components in Southern Ocean aerosols are even more scarce than inorganic measurements^{11,16,17}. Recently, the first yearlong measurements of organic functional groups in coastal Antarctic aerosols showed a seasonal trend with 150 times higher natural organics in summer than in winter. These natural organics were mainly attributed to marine and seabird emissions¹⁸.

The organic nitrogen (ON) component of marine aerosols represents one of the largest unknowns in aerosol composition and behavior, mainly due to the complexity of the ON pool and a lack of highly time-resolved and/or coupled ocean and atmosphere measurements^{19,20}. ON is considered a tracer species in Antarctica and has been studied through amino acid proxies in particles produced by bubble bursting at the air-sea interface^{21,22} and from the hatching of penguins^{23,24}. A comprehensive characterization of marine sources of aerosol ON is hampered by the lack and difficulty of synergistic measurements in the surface ocean and atmosphere.

Recently, by means of synergistic atmospheric and oceanic measurements in the Southern Ocean near Antarctica, we reported that the microbiota of sea ice and sea ice-influenced ocean can be a source of atmospheric ON, specifically low molecular weight alkyl-amines and nitrogen-containing osmolytes²⁵. One of the conclusions of that work was that there is the need for going beyond the use of surface chlorophyll *a* data as the sole predictor of marine organic nitrogen emissions, since identified nitrogen compounds did not co-vary with total phytoplankton pigment²⁵.

In this work, we advance the study of Dall'Osto et al. (2017)²⁵ by reporting a detailed analysis of single particle mass spectra. Alkylamines may comprise a small percentage of marine organic nitrogen but can effectively diffuse across the sea-air interface where they may affect the chemistry of the atmosphere, for example being one of the few semi-volatile compounds that reacts with sulfate and other acidic species in the atmosphere to form aerosol. For the first time, an aerosol time-of-flight mass spectrometer (ATOFMS) was deployed in Antarctica during more than 40 days, rendering the composition of single aerosols from ambient air as well as from a sea-spray generation chamber on board. Aerosol mass spectra were compared with measurements in surface seawater and melted sea ice, and were interrogated for the presence of alkylamines, their mixing state, and their primary or secondary origin.

2 Methodology

The cruise. The PEGASO (Plankton-derived Emissions of trace Gases and Aerosols in the Southern Ocean) cruise was conducted on board the RV Hesperides in the regions of Antarctic Peninsula, South Orkney and South Georgia Islands from 2 January to 11 February 2015.

Hydrographic measurements and seawater sampling. Thermosalinograph SBE 21 SeaCAT was used to record seawater salinity and temperature. Shipboard Acoustic Doppler Current Profiler (SADCP) "Ocean Surveyor" at 75 kHz was used to measure water current. Niskin bottles of the CTD rosette were used from a depth of 4 m to collect sea water samples.

Sea ice samples. Three sea ice samples were collected from a zodiac boat (selected for their brownish color indicating colonization by algae) on three different points during the field study at the northern and southern edge of the South Orkney Islands. Once on board of the RV Hesperides (A-33), the sea ice samples were melted (adding about 1/5 volume of sea water collected at the ship location near sea ice), and the melted sea ice introduced into the aerosol generator tank.

Atmospheric ambient sampling. The on-line instruments deployed on this study were housed inside the bow of the ship, an ad-hoc designed inlet (9 m in length and 1" outer diameter, with a PM_{2.5} cut-off at a flow rate of 5 L min⁻¹, overall residence time about 40 seconds) was used to collect aerosols via a laminar flow. Off-line parallel aerosol samples were taken on the ship upper deck by means of a multistage impactor (5-stages Berner impactor, type LPI80, Hauke). Ion chromatography used for the discussion of the pH and partitioning of amines (Table S1-S3) was used for the subsequent quantification of water soluble inorganic ions and low molecular weight alkylamines (methyl-, ethyl-, dimethyl-, diethyl- and trimethylamine) (Facchini et al., 2008).

ATOFMS. We used the ATOFMS (model 3800-100, TSI, Inc.) to collect bipolar mass spectra of individual aerosol particles^{26,27}. The ATOFMS is a particularly good aerosol instrument for studying amines and organic nitrogen in general because the LDI laser wavelength (266 nm) ionizes them very

efficiently²⁸⁻³⁰. ATOFMS single particle positive and negative mass spectra were imported into YAADA (Yet Another ATOFMS Data Analyzer) and single-particle mass spectra were grouped with adaptive resonance theory neural network, ART-2a³¹ (learning rate 0.05, vigilance factor 0.85, and 20 iterations). Further details of the parameters can be found elsewhere³².

Briefly, the ART-2a area matrix (AM) of a single particle mass spectra represents the average intensity for each m/z for all particles within a group, reflecting the typical mass spectra of specific aerosol groups.

Aerosol generation tank experiments. Seven open ocean water and three sea ice melt water samples (10 in total) were recirculated into plunging jet to generate bubbles and aerosols. By means of a square glass tank of 10 l (filled with 3 l of sea water or melted sea ice, air flow of 11 l min, described elsewhere³³), sprayed bubble-bursting aerosol size and composition was monitored with an ATOFMS.

Aqueous MA concentrations. Seawater samples (850 ml) were gravity-filtered through 47 mm GF/F filters into 1 L high density polyethylene (HDPE) bottles containing HCl (10 mL, 11.6 M, stored at 4 °C until analysis), then saturated with NaCl and adjusted to pH 13.4 with NaOH. Methylamines (mono-, di- and trimethylamines) were extracted from the water sample by solid phase microextraction³⁴, where polydimethylsiloxane/divinylbenzene fibre was exposed in the headspace above the water sample, for 2.5 h at 60 °C. Methylamines were resolved and detected using a GC with NP detector, calibrations carried out using external matrix-matched standard solutions containing mono-, di- and trimethylamine (0.13-13.3 nM).

Aqueous quarternary amine concentrations. Seawater samples (10 mL) were gravity filtered through 47 mm GF/F filters. The filters were flash frozen in liquid nitrogen and stored at -80°C until analysis. Nitrogen osmolytes (glycine betaine and choline) were extracted from filters in 12:5:1 methanol:chloroform:water spiked with internal standard (d_{11} GBT), and analysed by Liquid Chromatography/ Mass Spectrometry (LC/MS) according to Beale and Airs, 2016. Calibration was performed before each analysis using a calibration curve of solutions containing glycine betaine, choline and

internal standard. Check standards were also analysed after every 3 samples to check instrument response.

3 Results

3.1 Water and melted sea ice measurements

Fig. 1 shows the transit of the research vessel A-33 Hesperides (solid black line). The study region of this study is the Weddell / Scotia Sea, and the border between sea ice influence and ice-free waters was defined by the position of the Southern Boundary of the Antarctic Circumpolar Current (SBACC), situated around 60 °S (dotted black lines²⁵).

The nitrogen-containing osmolytes glycine betaine and choline were measured in particulates from surface seawater (mainly biota) collected at all stations in Fig. 1. Glycine betaine and choline are used as osmolytes by marine microbes³⁵, but can also act as a C, N or energy source for marine biota³⁶⁻³⁷. They are also precursors of methylamines³⁸, which are volatile components of the marine organic nitrogen pool. They are ubiquitous in marine systems, however little is known about their distribution, production and fate in sea waters. The average concentration of glycine betaine+choline in the ice-influenced region south of the SBACC was 97 nM, and the concentrations in this ice influenced region were significantly higher (Welch's t test; $p = 0.017$) than those observed north of the SBACC (average = 43 nM, Fig. 1.) The total methylated amine (monomethylamine + dimethylamine + trimethylamine) concentration was also higher south of the SBACC (Welch's t test; $p = 0.042$; average concentration = 6.06 nM) than north of the border (average concentration = 2.51 nM; Fig. 1). Total methylated amine concentrations were also measured in two of the three melted ice samples, being 6.49 and 10.84 nM, which were well above the average concentration for the ice-influenced water samples. Nitrogen osmolytes were not measured in ice samples. The melted sea ice measurements were carried out 24h after bubbling, at least after water recirculation for ice melting; as there was no

control on gas losses, it is very likely these measurements are underestimates, nevertheless still supporting the idea that sea ice is a source of these chemical compounds.

3.2 Aerosol chamber experiments

Mass spectra of particles generated by bubbling melted sea ice were compared with those produced by bubbling surface sea water. We already reported that ATOFMS single-particle information on the mixing state revealed that 21 % of the sea ice-derived particles were an internal mixture of sea salt with organic nitrogen and carbon, versus only 5 % in seawater spray²⁵. Here, we expanded the analysis by running ART-2a on the combined seawater and melted sea ice aerosol chamber dataset (approximately 7,000 single particle mass spectra). Initially 277 clusters were found but many were merged following procedures explained elsewhere³². Briefly, some of the main ART-2a clusters were very similar to each other. The main differences were due to the peak area or to the noise level³². For example, a problem encountered in the classification of different particle types arises from the miscalibration of some peaks (i.e. whilst the ATOFMS positive spectra are almost identical between two different classes, the negative one could only differ by a shifting of m/z 1 of spectra or few peaks). Although the reason for this miscalibration is unknown³², the issue was solved by merging the two different ART-2a clusters. Through this merge, the total number of clusters describing the complete primary aerosol chamber database was reduced to four that describe about 90% of the population of particles with both positive and negative spectra. The remaining 10% of the population with both positive and negative spectra were characterised by low-mass spectral resolution and having low overall signal/noise. The primary aerosol chamber ATOFMS measurements revealed unique organic nitrogen features in the mass spectra of individual particles, named "OC-CHN" (Organic Carbon - Amines), "OC-CHN-NaCl" (Organic Carbon - Amines - Sodium Chloride), "NaCl-OC-CHN" (Sodium Chloride - Organic Carbon - Amines) and "Ca-OC-CHN" (Calcium - Organic Carbon - Amines), altogether accounting for about 5-21 % of the ATOFMS particles

classified during aerosol chamber experiments (depending on the water type bubbled). The positive and negative ART-2a area matrices for the four particle types described, and the average size distributions (unscaled ATOFMS data³⁹) are shown in Fig.s 2 and S1, respectively.

All particles were internally mixed with Na (m/z 23), Mg (m/z 24), K (m/z 39) and Cl (m/z 35), consistent with the expectation that they were internally mixed with sea salt in sea spray. Peaks at m/z -111 and -129 were attributed to $[\text{NaCl}_2(\text{H}_2\text{O})]^-$ and $[\text{NaCl}_2(\text{H}_2\text{O})_2]^-$, respectively⁴⁰. The presence of water in pure sea-salt particles was confirmed by the presence of peaks at m/z -16 $[\text{O}]^-$, -17 $[\text{OH}]^-$, -46 $[\text{Na}_2]^-$, 62 $[\text{Na}_2\text{O}]^+$, and 63 $[\text{Na}_2\text{OH}]^+$. The negative ion mass spectrum shows prominent peaks at m/z -26 $[\text{CN}]^-$ and m/z -42 $[\text{CNO}]^-$, indicating that all particle types presented were internally mixed with organo-nitrogen species (Fig. 2). These major peaks were seen in all single particle mass spectra and are not further described. However, some of the particle types presented more distinct peaks, hence the naming of the four particle types .

- OC-CHN (Organic Carbon- Amines): Fig. 2a shows the ATOFMS mass spectra of a particle type called OC-CHN. Based on previous studies, the peak at m/z 59 ($[\text{N}(\text{CH}_3)_3]^+$) was attributed to trimethylamine (TMA)^{28,29}. With a tertiary-substituted N atom, TMA is the most basic of the methylated amines and plays an important role in atmospheric chemistry, yet its pathway towards aerosol is not clear. Rehbein et al. (2011)⁴¹ demonstrated that cloud/fog processing could enhance gas-to-particle partitioning of TMA. TMA can also participate in the formation of secondary organic aerosol. Several studies have shown that gas-phase TMA could form non-salt organic aerosol products through reaction with oxidizing agents⁴². However, in this study, we detected TMA in primary-generated aerosol particles; furthermore, the analysis of water samples also revealed the presence of TMA, and compounds that could readily produce TMA (eg. glycine betaine). Other peaks associated with amines included m/z 72, 74 and 86. A common characteristic of the diethylamine (DEA) spectra is the presence of ion peaks at m/z 70, 72, and 74²⁸. Fragment ions at m/z 86 and 114 are associated with two or more alkylamines. The m/z 86 fragment ion may

also be associated with triethylamine (TEA) and dipropylamine (DPA), but has also been identified with other alkylamines products (Angelino et al., 2001). This ATOFMS OC-CHN particle type also presents peaks at m/z 27 $[C_2H_3]^+$ and m/z 43 $[(CH_3)CO]^+$ usually associated with oxidized organic aerosol⁴³. Finally, the unique presence of peaks at m/z -45, -59 and -71 are likely to be due to the formate $[CHO_2]^-$, acetate $[C_2H_3O_2]^-$ and propionate $[C_3H_5O_2]^-$ ions, respectively³⁰. In summary, particle type OC-CHN was characterized by the highest amount of organic peaks both in the positive and negative mass spectra, and distributed in the smallest size bins at about 0.5 μm (Fig. S1).

- OC-CHN-NaCl (Organic Carbon - Amines - Sodium Chloride): Fig. 2b shows the ATOFMS mass spectra of a particle type called OC-CHN-NaCl. Relative to the previous one, this type shows a presence of a peak at m/z 81 $[Na_2Cl]$, usually considered as a marker for NaCl⁴⁰. Peaks due to organic species were very minor in the negative spectra. By contrast, peaks at peak -79 and -80 can be seen, possibly due to $[PO_3]^-$ and $[SO_3]^-$, respectively. Fig. S1 shows an average size distribution peaking at about 0.8 μm .
- NaCl-ON-CHN (Sodium Chloride - Organic Carbon - Amines): Fig. 2c shows the ATOFMS mass spectra of a particle type called NaCl-OC-CHN. Major peaks can be seen for sea spray due to $[Na_2Cl]^+$ (m/z 81 and 83), and $[NaCl_2]^-$ (m/z -93, -95 and -97), respectively, in the positive and negative mass spectra. This was confirmed by the larger average size distributions (Fig. S1) where supermicron particles were present.
- Ca-OC-CHN (Calcium - Organic Carbon - Amines): Fig. 2d shows the ATOFMS mass spectra of a particle type called Ca-OC-CHN. This particle type showed very different average mass spectra both in the positive and negative mass mode. In the positive spectra, strong peaks associated with calcium (m/z 40 $[Ca]^+$, 56 $[CaO]^+$, 57 $[CaOH]^+$ and 96 $[Ca_2O]^+$) were present. Peaks associated with sodium (m/z 23), magnesium (m/z 24, 25) and potassium (m/z 39) could also be seen.

These particles were, on average, the largest submicron organic nitrogen-containing particles detected in this study (Fig. S1).

The ATOFMS single particle mass spectra collected during the primary aerosol chamber experiments revealed that all the amine-containing particles were internally mixed with sea spray, although larger supermicron particles showed stronger influence of sea spray and likely other Ca-rich components. The enrichment of calcium may be possibly related to marine polymeric gels, which are produced by phytoplankton and sea ice alga secretions and can be transferred by bubble bursting from the sea-air interface into the polar atmosphere^{44,45}. These biopolymers are inter-bridged with divalent cations (Ca^{2+} and Mg^{2+}) to which other organic compounds, such as proteins and lipids, are readily bound, resulting in a gel-like consistency⁴⁶.

3.2 Aerosol ambient data

The deployment of single-particle mass spectrometers already proved useful in the identification of alkylamines in ambient aerosol in real time, and have also enabled investigation of their mixing state²⁹. Alkylamines have been detected in ambient air using single-particle mass spectrometers in a variety of locations, including the continental USA⁴⁷, Canada⁴¹, China^{48,49}, Mexico⁵⁰ and Europe²⁹. It is interesting to note that in a marine location in Corsica (France), all alkylamines detected in particles were also found to be internally mixed with methanesulfonic acid, indicating that aminium methanesulfonate salts may represent a component of marine ambient aerosol in the summer months²⁹. In remote marine conditions, Dall'Osto et al. (2012)⁵¹ reported nitrogenated and aliphatic organic vapors as possible drivers for marine secondary organic aerosol growth. Recently, Kollner et al (2017)⁵² reported that a significant fraction (23%) of the single particles sampled in the Canadian high Arctic lower troposphere contained trimethylamine originating from marine biogenic emissions.

Our ATOFMS mass spectra of ambient aerosols in the areas of the Antarctic Peninsula, South Orkney and South Georgia Islands revealed that

alkylamines were present in about a quarter of the particles containing organic species. We then associated ATOFMS mass spectra with different air mass trajectory histories, specifically “open water” (OW) and “sea-ice” (SI) source regions, according to the characteristics of the area overflow²⁵. The results are shown in Fig. 3: ice-influenced air masses showed a strong enhancement of ON-containing peaks relative to those from the open ocean. When the ON-containing ATOFMS spectra were interrogated for the presence of sea salt, only 11-25 % corresponded, suggesting most of the amines were of secondary origin. The non-negligible % of sea salt, however, also suggests the contribution of primary N-containing aerosol carried by sea spray. The action of wind friction on the surface ocean generates air bubbles that scavenge colloidal and particulate organic matter, including proteinaceous gels, bacteria and viruses, and release them into the atmosphere by bursting^{21,22}. It is worth noting that the majority of the ambient ATOFMS spectra contained a main peak at m/z 114, which may be assigned to dipropylamine or tripropylamine^{28,29}. This peak was not seen in ATOFMS positive mass spectra from the generated primary aerosols reported (Fig. 2). The marker ion at m/z 114 has previously been demonstrated to be preserved in particles that contain amine salts and which have been subjected to photo-oxidation^{29,30}. Further studies are needed to understand more about the origin of the peak at m/z 114 and why it was not seen in aerosol tank experiments. It is likely that unknown photo-oxidative processes could be converting ON primary species into the ambient atmosphere ones responsible for the peak at m/z 114. An example of a single particle mass spectrum collected in the open ocean ambient air is shown in Fig. S2. Air mass back trajectories²⁵ showed that this aerosol travelled mainly over open pack sea ice (77 % of the time), over open sea (23%) and never over land. Peaks at m/z 59, 74 and 114 (alkylamines peaks of $[(CH_3)_3N]^+$, $[(C_2H_5)_2NH_2]^+$, $[(C_3H_7)_2NCH_2]^+$, respectively²⁸) dominated the positive mass spectra. In the negative mass spectra, peaks due to oxalate (m/z -89, $[(C_2O_4H)H]^-$) and to a lesser extent sulfate (m/z -97 $[SO_4]^{2-}$) could be seen. The small peak at m/z 179 is attributed to the oxalic acid dimer $[(C_2O_4H)_2H]^-$, which is commonly observed in the spectra of oxalic acid standards. This supports the fact that the peak at m/z -89 can be predominantly attributed to oxalic acid⁵³. Other peaks at high

m/z in both positive and negative mass spectra could not be identified. The minor presence of inorganic peaks suggests that this particle type had a high degree of organic material, likely formed via secondary processes.

4 Discussion and conclusion

Ocean water-melted sea ice measurements and aerosol generation tank experiments. Here, we have provided data showing that ice-influenced surface waters are enriched in alkylamines and their precursors, the algal osmolytes glycine betaine and choline (Fig. 1). In the current study - by a complete analysis of single particle mass spectra from bubbling tank experiments with melted sea ice, ice-influenced and non-ice-influenced sea waters - demonstrates that the sympagic environment (i.e., sea ice and sea ice-influenced sea waters) is more likely to supply alkylamines in sprayed aerosols than open ocean pelagic water. Single particle mass spectrometry helps determine how different chemical constituents are distributed among particles (namely, the mixing state). The aerosol mixing state in turn can affect droplet formation when the resulting hygroscopicity distribution is sufficiently heterogeneous⁵⁴. The mass spectra of an aerosol population can be defined as the degree of homogeneity in the distribution of the chemical components within it⁵⁵. Thus, an aerosol population can be broadly defined as “internally mixed” when each single particle presents the same chemical composition, which equals the bulk composition), or “externally mixed” when particles of different chemical composition co-occur. All the generated primary aerosols were internally mixed with sea salt within the detectable ATOFMS size range (about 350-1350 nm). Both DMA and TMA were identified in the mass spectra of these internally mixed aerosols (Fig. 2a-d), suggesting that the alkylamines were part of the dissolved organic matter sprayed by bubble bursting. A subset of coarser particles contained alkylamines internally mixed with calcium, which could originate from algae or other biological samples in the form of particulate organic matter such as marine polymeric gels (Fig. 2d).

Atmospheric ambient sampling. In the clean, marine Antarctic atmosphere, the particle number concentration of primary and secondary aerosols is mainly driven by the seasonality of biological productivity in the Southern Ocean^{16-17, 56-59}. The mechanisms, however, for the production of either primary or secondary biogenic aerosols are not fully clarified. In our ambient aerosols study, about a fourth of the detected and analyzed particles collected in Antarctic air masses over a period of about 40 days contained alkylamines. Most of them (75-89 %), were externally mixed with sea spray and likely were of secondary origin.

Based on the effective Henry's law Constant (K_H) of TMA at 278 K, reported by Leng et al. (2015)⁶⁰, and on the observed concentrations of TMA in seawater (4.2 nM), we estimate an equilibrium gas phase concentration of 110 pmol m⁻³ over the sea-ice influenced zone. The concentrations of TMA⁺ determined in the aerosol phase were 13.5 pmol m⁻³, about one order of magnitude lower than those estimated in the gas phase. TMA (and other low-molecular weight alkylamines as well) is water-soluble and semi-volatile, so it tends to partition between the gas and aerosol phase as dictated by equilibrium thermodynamics. Similar to its inorganic counterpart ammonia/ammonium, TMA tends to increasingly partition to the aerosol as temperature decreases, and, aerosol LWC & acidity increases. Antarctic aerosol, owing to its low dry aerosol loading, tends to have low aerosol concentration (hence LWC); nevertheless, a significant fraction of alkylamines may still reside in the aerosol, if it is acidic enough⁶⁰. To demonstrate this, we apply the gas-particle partitioning equation by Leng et al. (2015), based on a pH-dependent formulation of the K_H . Aerosol liquid water content (LWC) and pH were calculated by the ISORROPIA-II model^{61,62} using the chemical composition of ambient aerosol already described in Dall'Osto et al. (2017)²⁵, the ambient air Temperature (T) and Relative Humidity (RH) measured during the cruise (see Table S1-S3). Aerosol LWC and pH resulted in average values of 0.65 $\mu\text{g m}^{-3}$ and 1.4, respectively, over the sea-ice influence zone. Under such conditions, a transfer of 13% of TMA is expected to partition in the particle phase. These calculations demonstrate that the concentrations of alkylamines measured in the ambient aerosol and in the surface ocean waters are consistent with equilibrium partitioning theory. They

also demonstrate that a flux of low molecular weight alkyl amines from seawater to the atmospheric gas phase and subsequent condensation onto acidic sub-micron particles is possible over the Weddell Sea – and in fact will *only* partition to the most acidic of submicron particles (ultrafines). The presence of TMA also further supports the thought that marine aerosol is strongly acidic, which in itself carries important implications for the processes that determine the bioavailability of trace nutrients and metals in submicron aerosol.

Organic nitrogen sources in the Antarctic region. Little is currently known of the role of the atmosphere in redistributing nitrogen species across marine ecosystems. Dall'Osto et al. (2017)²⁵ reported ambient aerosol concentrations of sub-micrometer low molecular weight amines, of 7.1 (± 1.8) and 1.5 (± 0.8) ng m⁻³ for the “sea-ice” and “open-water” source regions, respectively, during the cruise object of the present study. The total amine concentration resulted from five detected species, namely methylamine (MA⁺), ethylamine (EA⁺), dimethylamine (DMA⁺), diethylamine (DEA⁺) and trimethylamine (TMA⁺), with DMA⁺ and DEA⁺ being the most abundant in both regimes. The DMA⁺ concentration reported for the “sea-ice” region (2.0 ± 0.4 ng m⁻³) is comparable to those reported by Gibbs et al. (1999)⁶³ for the Arabian sea (August-October 1994) but lower (from 5 to 60 times) than the values reported for the North Atlantic ocean, during the high biological activity period¹⁹, and for the marginal seas of China^{64,65}. Lower concentrations (about one order of magnitude) than those observed over the Weddell Sea were reported by Müller et al. (2009)⁶⁶ at Cape Verde (tropical Atlantic waters). Similarly, DEA⁺ concentration (3.8 ± 1.0 ng m⁻³) over the Weddell Sea is lower than mid-latitude North Atlantic ocean concentrations¹⁹ and higher than Tropical Atlantic ocean ones⁶⁶. Literature data for TMA⁺ concentration in the marine environment are available for the Arabian Sea⁶³ and for the marginal seas of China^{65,66}, with the latter having almost three orders of magnitude higher concentrations than the former; the average concentration of TMA⁺ observed over the Weddell Sea (0.8 ± 0.3 ng m⁻³) falls within the range of the previous observations. The average alkylamines/NH₄⁺ molar ratios observed in the “sea-ice” and “open

sea" source regions were 0.03 and 0.02, respectively, falling in the range of literature reported values.

The pioneering study of Legrand and Ducroz (1998)⁶⁷ discussed the influence of polar ocean and penguin emissions on ammonium concentrations in coastal Antarctica. Atmospheric ammonium concentrations were quite variable, with a summer maximum ranging from 12.5 to 140-260 ng m⁻³. The emissions from the penguin population would not seem to be a major source, yet ammonia emission all over Antarctica was considered uncertain. Aerosol produced by ornithogenic soil emissions may contain oxalate, which may be produced together with ammonium by bacterial decomposition of uric acid. This may permits the subsequent loss of ammonia - and likely other volatile organic nitrogen compounds - to the atmosphere^{23,67,68}. As mentioned earlier, a "marine" and a "seabird" source were also identified in the southern tip of Ross Island¹⁸. The marine source was identified by its high hydroxyl group fraction, and the seabird source by its fingerprints of ammonium and organic nitrogen, they constituted the main sources of CCN in the remote marine boundary layer. During our study, alkylamines detected in ambient air were associated with air masses that had previously travelled over the ice-covered Weddell Sea and its marginal zone of ice-influenced ocean, along with some spots around the Antarctic Peninsula and the South Georgia phytoplankton bloom²⁵, excluding coastal penguin emissions. Given that our study was carried out in open ocean regions, it is not surprising that there was little influence from coastal penguin emissions. Further studies are needed to apportion the relative importance of bird colonies and sympagic/pelagic open ocean water. We found that some alkylamines of secondary origin were associated with oxalic acid (Fig. S2). Since oxalate is generally thought to arise from aqueous phase oxidation, future work will address the sources of oxalic acid and its mixing state in the Antarctic atmosphere.

In the marine environment, low molecular weight aliphatic amines usually have gas-phase concentrations that are about two orders of magnitude lower than that of ammonia (NH₃); however, these species are more basic than NH₃, which makes them better suited to neutralize strong acids like sulfuric and methanesulfonic and stabilize molecular clusters that may lead to new particle formation⁶⁹. Currently, very little is known about the

relative gas phase concentrations of ammonia and amines in the Antarctic regions, such measurements would be highly valuable. Almeida et al. (2013)⁷⁰ demonstrated that atmospheric concentrations of DMA could enhance particle-formation more than 1,000-fold compared with ammonia, enough to account for the observed atmospheric particle-formation rates. Hence, given the low particle number concentrations reported in Antarctic regions^{71,72}, alkylamines could play a role in particle formation by nucleation. Further studies, with instruments capable of resolving the composition of molecular clusters⁷³, are needed to confirm or reject this suggestion.

Very few studies have measured the chemical composition of aerosols in the summertime Antarctic. Here we should that (a) high concentrations of alkylamines can be found in melted sea ice and sea-ice-influenced waters; (b) they could result from degradation of quaternary amine osmolytes, which we also found in sympagic plankton; (c) sea-spray generation experiments showed that alkylamines were internally mixed with sea salt, hence they are carried by sea spray into primary aerosols; (d) in ambient air, they were mostly externally mixed with sea salt and hence, of secondary origin; (e) thermodynamic equilibrium calculations suggest their shift from primary to secondary aerosol tends is driven by the large pH gradient seen between fine and ultrafine particles; (f) air mass back trajectory analysis exclude a major association with bird emissions. Our study points to sea ice and surrounding microbiota being an important and overlooked contributor to aerosols through emissions of volatile and non volatile organic nitrogen, including alkylamines. Further data in these undersampled remote oceanic regions - both from mobile and fixed platforms - are needed in order to correctly apportion the role of sympagic and pelagic waters, seabirds and mammals as atmospheric nitrogen sources in the Antarctic and Southern Ocean atmosphere. Understanding how alkylamines interact to form aerosols, may be one of the important missing pieces to accurately forecast aerosol production around Antarctica, including possibly how re-evaporation of amines from the aerosol phase may help promoting new particle formation.

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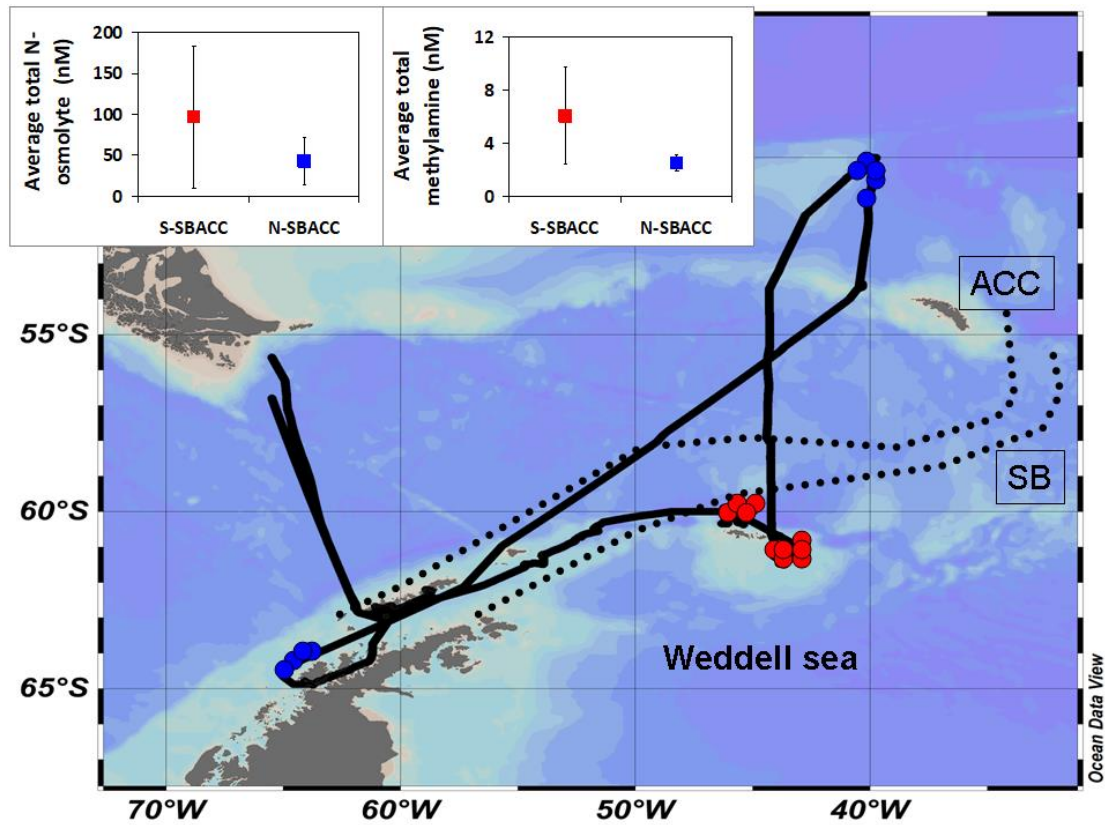
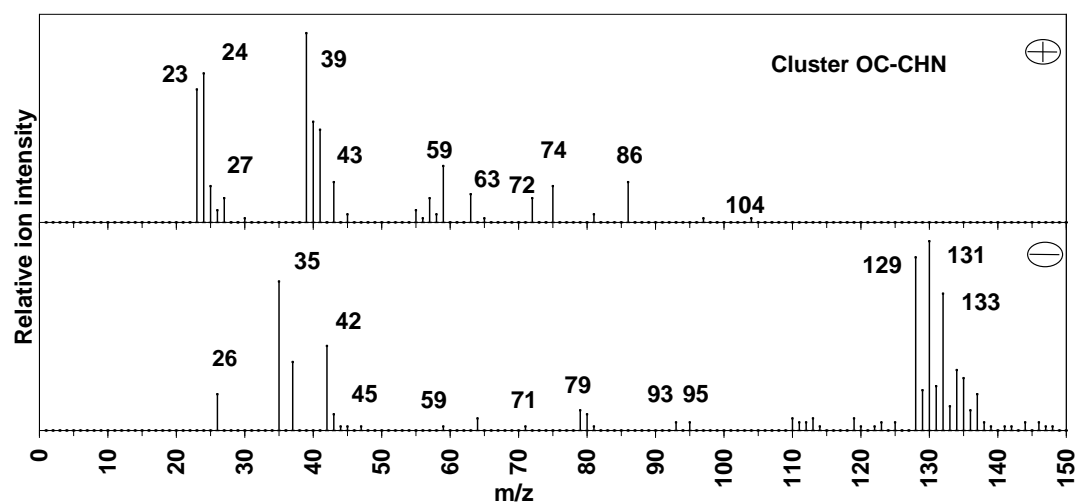
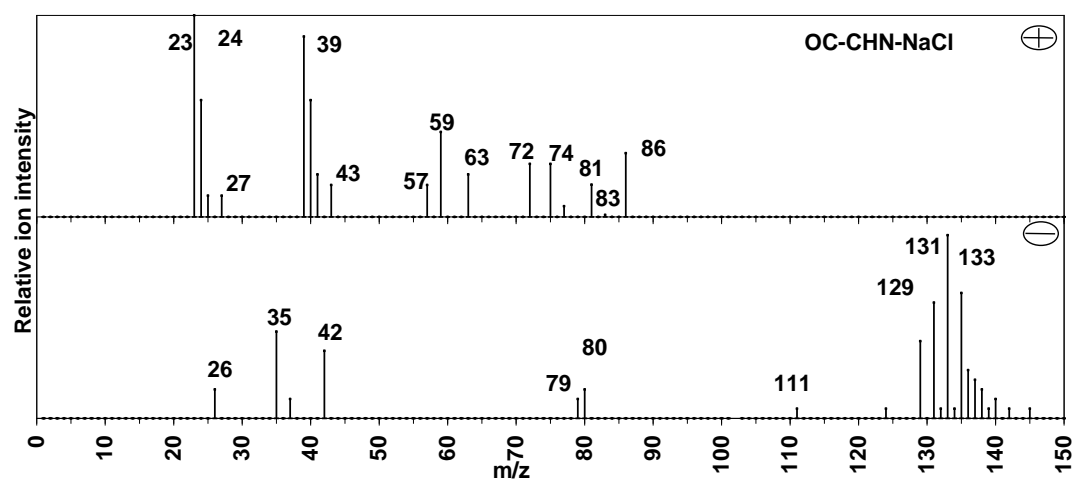


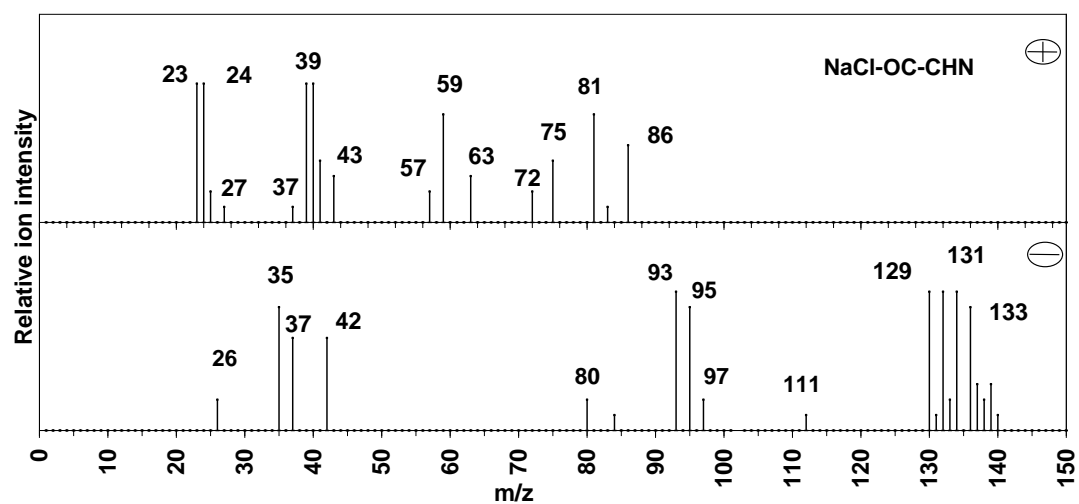
Fig. 1 Map of the study region. The black solid line is the cruise track. Approximate synoptic locations of the main hydrographic fronts are indicated with dashed lines: Antarctic Circumpolar Current (ACC) and Southern Boundary (SB). SBACC stands for Southern ACC and SB fronts. In red dots are water sampling stations south of the SBACC, whereas in blue are stations north of the SBACC. Top Fig.s: concentrations (average, standard deviation) of particulate N-osmolytes and dissolved alkylamines in surface seawater. Average total N-osmolyte concentration (glycine betaine+choline; red), and average total methylamine concentration (monomethylamine + dimethylamine + trimethylamine; blue) are shown south (S) and north (N) of the southern boundary of the Antarctic Circumpolar Current (SBACC).



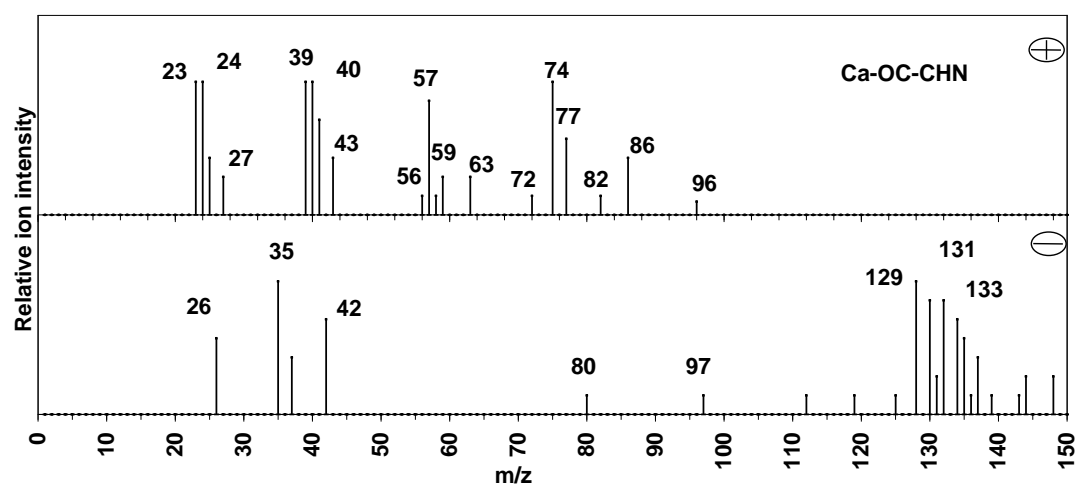
(a) OC-CHN



(b) OC-CHN-NaCl



(c) NaCl-OC-CHN



(d) Ca-OC-CHN

Fig. 2 Positive and Negative ART-2a area vectors attributed to (a) OC-CHN, (b) OC-CHN-NaCl, (c) NaCl-OC-CHN and (d) Ca-OC-CHN.

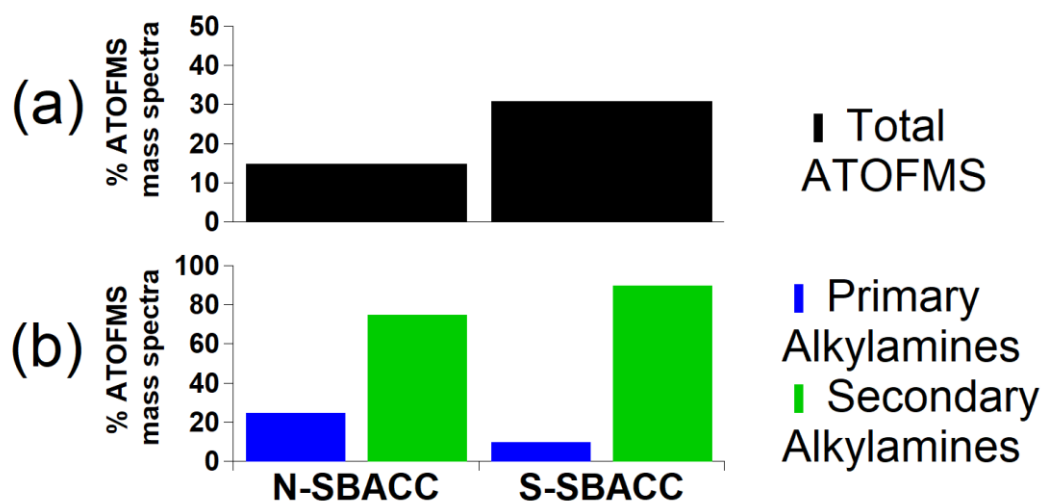


Fig. 3 Percentages of the total number of ATOFMS organic particles containing alkylamines; detected from air masses originated in North and South SBACC fronts (a) and percentages of these particles internally mixed with sea spray (b), respectively.

SUPPORTING INFORMATION

Figure S1-S2: aerosol size distributions and mass spectra of ATOFMS

Table S1-S3: Alkylamines-ions concentrations and selected variables during the PEGASO cruise

“For TOC Only”.

